Optical cooling in $Er^{3+}:KPb_2Cl_5$

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Abstract: For the first time, optical cooling has been observed in the $^4I_{13/2}$ excited state of erbium(III), using the low phonon energy host materal, potassium lead chloride (KPb_2Cl_5). Cooling was observed when samples were pumped at wavelengths longer than 1557 nm, 17 nm longer than the mean fluorescence wavelength of 1540 nm, which implies a nonradiative heat load of 1.1% for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. When pumped at 1568 nm, the total cooling efficiency was 0.38% of the absorbed power. These results highlight the potential of $Er^{3+}:KPb_2Cl_5$ as a material for lasers operating in an eye safe spectral region.

OCIS Codes: (160.3380) Laser materials; (160.5690) Rare-earth-doped materials; (140.3500) Lasers, erbium; (140.3320) Laser cooling

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1. Introduction

Over the last decade or so, there has been a great deal of interest in the optical cooling of materials by anti-Stokes fluorescence. If a chromophore absorbs a photon whose energy is below its average emitted photon's energy, then the energy difference is extracted from the system and cooling can occur. This effect was first described in 1929 [1], but it was not observed experimentally until experiments on gaseous CO_2 were reported in 1981 [2]. The first observation of anti-Stokes cooling in a solid, Yb^{3+}:ZBLANP glass, was reported in 1995 [3], followed by observations of cooling in Tm^{3+}:ZBLANP [4] and in the crystalline materials Yb^{3+}:KGd$(WO_4)_2$ [5] and Yb^{3+}:YAG [6]. Typical reported cooling efficiencies are small, with cooling powers of < 3% for the ytterbium-doped materials.

While much of the work in optical cooling of solids has focused on its potential applications in cryocooling [7], other work has shown the utility of anti-Stokes fluorescence cooling in removing heat from laser media [8, 9]. This work so far has focused on ytterbium-doped materials lasing near 1 μm. It would be desirable, however, to make similar high-power sources in the "eye safe" spectral region beyond 1.4 μm. An obvious ion for such a source is erbium (III), whose $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition emits light at ~1.5 μm and has served as the basis for many lasers. There has been a substantial amount of recent work on resonant or near-resonant pumping of this transition in Er:YAG [10-13] in order to reduce heat loading due to the quantum defect and increase power. In most hosts, however, there is a tendency for excitations into this state to upconvert to the $^4I_{9/2}$ state, which, when it nonradiatively relaxes to the $^4I_{11/2}$ state, generates heat. Potassium lead chloride (KPb_2Cl_5) has the potential to overcome the upconversion problems. Er:KPb_2Cl_5 can be grown with high optical quality [14], and lasing has been demonstrated in it [15]. There has also been one report of optical cooling in this system from the $^4I_{9/2}$ state [16]. Its low phonon energy and uniquely low upconversion rates [17] promise to strongly mitigate heating from upconversion and nonradiative relaxation.

Previous measurements of optical cooling have typically been made using photothermal deflection spectroscopy or observation with a thermal camera. The latter method is inappropriate for KPb_2Cl_5, because the material is completely transparent in most of the mid-infrared and is therefore invisible to the thermal camera. Photothermal deflection is also problematic for several reasons. It requires laser sources and sample material of very high optical quality, and changes in the index of refraction of the sample due to excited-state population changes can confound the result and lead to false cooling signatures [18, 19]. It is also inherently limited to probing one small region of a sample, defined by the probe laser, at a time, so there is no guarantee that the probed region is representative of the sample as a whole. To avoid these problems, the data presented here employ direct measurement of a well-insulated sample in an evacuated chamber using a fine wire thermocouple. This allows for the direct and unambiguous measurement of the temperature of the entire sample.

2. Experimental

Samples of single-crystal, laser-grade Er:KPb_2Cl_5 were grown using a modified Bridgman method similar to that described previously [14]. To improve optical quality, zone-refined KPb_2Cl_5 was used in the initial charge and an extended cooldown routine was employed. The

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resulting boule, with an Er^{3+} concentration of 3.6×10^{19} cm^{-3} (as determined by comparison of the absorption strength with the known cross sections) was cut and turned to produce a rod 3 mm in diameter and 13.6 mm long with a polished barrel and end faces. The rod was aligned such that its axis was parallel to the [1 0 0] lattice pole, and all data were collected with the pump laser polarization oriented parallel to [0 1 0]. The specific heat of the material was measured to be 0.3 J g^{-1} K^{-1} using direct calorimetry by immersion of heated sample in n-heptane. Fig. 1 shows the previously-published absorption spectrum [20] of the sample polarized parallel to [0 1 0] and emission spectrum [17] averaged over all orientations; the average emission spectrum is shown since the fluorescence will be radiated in all orientations for any orientation of pump. The mark at 1539.8 nm denotes the fluorescence line center.

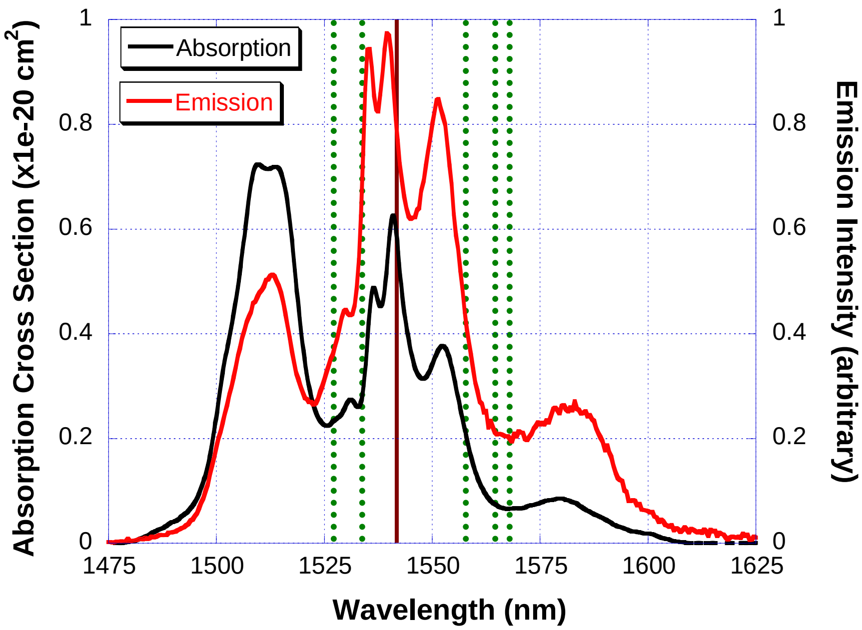

Fig. 1. Absorption (parallel to [0 1 0]) and emission (averaged over all orientations) spectra of $Er:KPb_2Cl_5$. The five dotted vertical lines denote the five pump diode center wavelengths used in the experiment, while solid vertical line denotes the fluorescence line center, λ_F = 1539.8 nm.

Three diode lasers (nLight NL-C-1.0) with different nominal wavelengths were used as pump sources. Two of the diodes were run at two different temperatures (15°C and 29°C) while the third was operated only at 29°C, to provide a total of five measured wavelengths. The spectra of each diode at the appropriate operating temperatures were recorded with an optical spectrum analyzer (ANDO 6317B); spectral linewidths were 4-7 nm. The center wavelengths of these diodes are shown in Fig. 1 overlaid on the absorption and emission spectra. For each measurement, the laser in use was collimated with a cylindrical and a spherical lens, focused through a 1 mm pinhole to improve the beam quality, then refocused onto the sample with a beam diameter of 1 mm.

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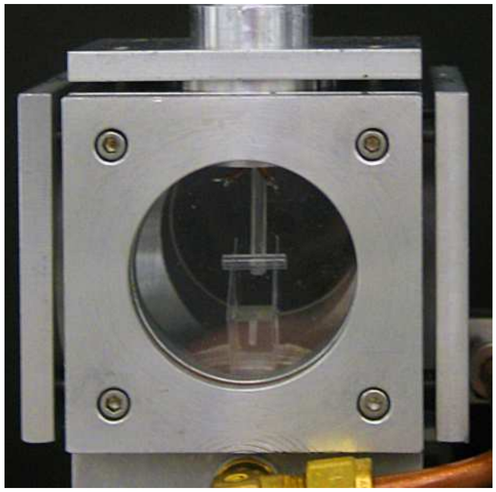

Fig. 2. The vacuum chamber with the sample and sample mount. The chamber itself is aluminum, with calcium fluoride windows on all four sides. The sample mount is made from two pairs of crossed glass cover slips mounted on a polycarbonate block to provide minimal thermal contact with the sample. The pump beam enters from the left and exits to the right.

The sample mount consisted of two pairs of crossed soda-lime glass cover slides attached to a polycarbonate post set inside an evacuated sample chamber (approximately 70 mm on a side) with 50 mm diameter by 6.5 mm thick CaF_2 windows on four sides; a photograph of this chamber is shown in Fig. 2. A power meter (Scientech AC2500) was placed on the other side of the chamber to measure the transmitted laser power. The absorbed power was calculated from the transmitted power (corrected for reflection losses) using the absorption spectrum of the sample and the emission spectra of the laser diodes. A fine wire (0.001" diameter) T-type (copper/constantan) thermocouple was positioned to contact the sample near its center, and its complementary junction was held in an isothermal block to prevent room temperature drifts from affecting the signal. The use of a fine wire thermocouple prevents heat transfer through it and improves its response time. In order to measure changes in the apparent temperature of the sample's surroundings, a second T-type thermocouple (with its complementary junction in the isothermal block) was placed in the chamber near the sample, but not in contact with it. The thermocouple voltages were measured with a picovoltmeter (Hewlett-Packard 34420A), and the signal from the analog output of the picovoltmeter was recorded using the high-resolution mode of a digital oscilloscope (Tektronix TDS744A).

For each measurement, the sample was exposed to the laser for ~6 minutes, or until thermal equilibrium was reached. A very small amount of visible (green) upconversion could be observed while the laser was illuminating the sample, although no attempts were made to measure it. The laser was then shut off and the temperature was recorded at 0.2 s intervals for 200 s. This measurement was performed five times at each measured wavelength and the resulting traces were averaged. Collection of the data as the sample relaxes back to equilibrium with the environment, rather than collection while the sample is illuminated, eliminates potential problems due to short-term drifts of the pump laser or errors due to illumination of the measurement thermocouples by fluorescence and stray pump light.

3. Results and discussion

The measured thermal transients were analyzed with a simple model, based on a previous one developed for analyzing photothermal deflection results [5,21]. As the crystal was in a vacuum chamber and in very weak conductive contact with its mount, the heat transfer is assumed to be completely radiative and the data were fit to a single exponential:

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$$\Delta T(t) = \Delta T_{eq} \exp\left(\frac{-t}{\tau}\right) \tag{1}$$

where t is the time since the laser turnoff, $\Delta T(t)$ is the change in temperature from ambient, ΔT_{eq} is the equilibrium ($t = \infty$) change in temperature, and τ is the thermal time constant of the sample. The fraction of the absorbed power that is converted into heat by the sample, ξ, can then be calculated:

$$\xi = \frac{mc_p \Delta T_{eq}}{\tau P_{abs}} \tag{2}$$

where m is the mass of the sample, c_p is its specific heat, and P_{abs} is the amount of power absorbed by the sample. This equation assumes that the temperature of the crystal is spatially uniform, a valid assumption given the small size of the sample and the small fraction (<15%) of pump power absorbed by the sample. As a function of pump wavelength, λ_P, the fractional heat load is given by:

$$\xi(\lambda_P) = \xi_{QD}(\lambda_P) + \xi_{NR}(\lambda_P) \tag{3}$$

where ξ_{NR} is the heat load due to nonradiative losses and ξ_{QD} is the heat load due to the quantum defect. ξ_{NR} is simply the (pump wavelength independent) complement of the radiative quantum efficiency, η:

$$\xi_{NR} = 1 - \eta \tag{4}$$

ξ_{QD} is given, in terms of the mean fluorescence wavelength, λ_F, by:

$$\xi_{QD}(\lambda_P) = \frac{\eta E(\lambda_P) - \eta E(\lambda_F)}{E(\lambda_P)} = \eta\left(1 - \frac{\lambda_P}{\lambda_F}\right) \tag{5}$$

We may define the crossover wavelength, λ_0, as the wavelength where, as λ_P is tuned from blue to red, the sample switches from net heating to net cooling:

$$\xi(\lambda_0) = 0 \quad \Rightarrow \quad \lambda_0 = \frac{\lambda_F}{\eta} \tag{6}$$

Substituting Eq. (4), Eq. (5), and Eq. (6) into Eq. (3) gives:

$$\xi(\lambda_P) = 1 - \frac{\lambda_p}{\lambda_0} \tag{7}$$

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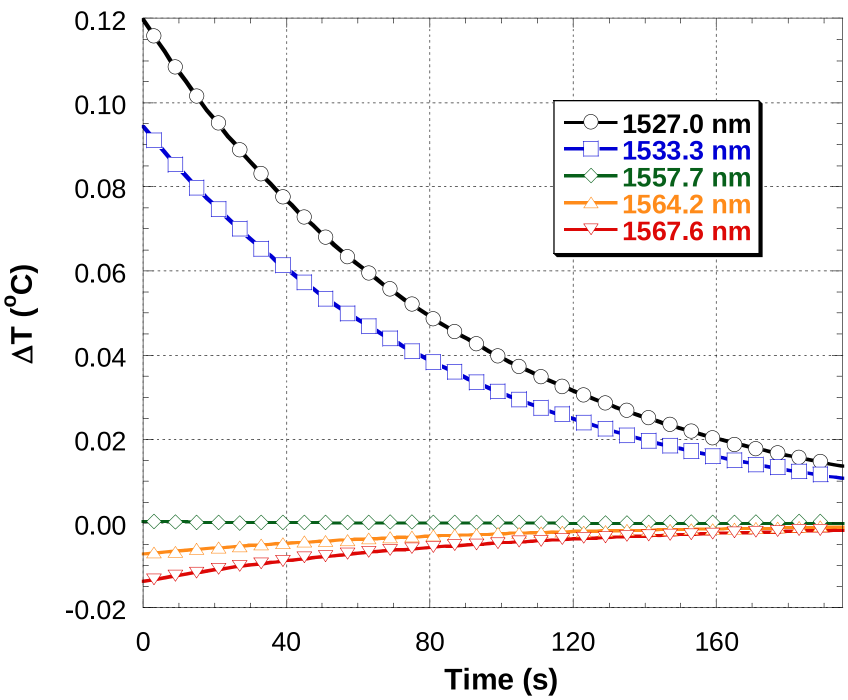

Fig. 3. Temperature transients, corrected for chamber temperature drift, following shutoff of the pump lasers. Every thirtieth data point is plotted, and each transient is fit to an exponential. The two shorter-wavelength curves show evidence of heating, while the two longer-wavelength curves show cooling.

Table 1. Temperature transient fitting results and the resulting calculated heat loads.

λ_{laser} (nm)	P_{abs} (mW)	ΔT_{eq} (C)	Heat Load
1527.0	20.3	0.1205	0.90%
1533.3	21.8	0.0943	0.66%
1557.7	18.9	0.0000	0.00%
1564.2	7.4	-0.0072	-0.15%
1567.6	5.3	-0.0136	-0.38%

Figure 3 shows the averaged temperature transients recorded after the pump laser was shut off at the five measured pump wavelengths. Measurements of the chamber temperature (using a non-contacted thermocouple inside the chamber) showed a drift with time after shutoff of the pump lasers that was consistently linear, but inconsistent in value from run to run. Given this, each temperature transient was fit to the sum of a linear term (to account for the behavior of the chamber) and an exponential term of the form given in Eq. (1). For the sake of clarity, the data shown in Fig. 3 were corrected for the sample drift term, and only the exponential part is shown. Based on the results from fitting the strongest signals, the time constant, τ, was set to 90 s for all fits.

Table 1 summarizes the results of the fits, all of which were of very high quality ($R^2 >$ 0.997). From the fit value for ΔT_{eq} at each wavelength, the fractional heat load was calculated using Eq. (2). The data from the two shorter wavelengths, 1527.0 nm and 1533.3 nm, show that heating occurred, with 0.90% and 0.66%, respectively, of the absorbed pump energy transferred to heating. The middle wavelength, 1557.7 nm, produced a nearly linear transient,

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suggesting that this diode is near the crossover wavelength. The two longest wavelengths, 1564.2 nm and 1567.6 nm, both showed cooling, with cooling efficiencies of 0.15% and 0.38%, respectively. No attempt was made to account for radiation trapping; given the low optical density of these samples ($\alpha < 0.15\ cm^{-1}$) and their narrow radius (1.5 mm), the effect of trapping should be negligible.

Figure 4 shows the measured fractional heat load of the sample plotted as a function of wavelength. The data fit well ($R^2 = 0.99$) to a line with a slope of $2.97 \times 10^{-4}\ nm^{-1}$ and a crossover wavelength of 1557 nm. The mean fluorescence wavelength for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was calculated to be 1539.8 nm. From (7), assuming 100% quantum efficiency, this would imply a slope of $6.49 \times 10^{-4}\ nm^{-1}$, significantly greater than the observed value. This result suggests that excited states other than $^4I_{13/2}$ are important to the observed heat load, and that further study is required to pin down the mechanisms of heating and cooling in this material. The crossover wavelength of 1557 nm implies a nonradiative fractional heat load of 1.1%.

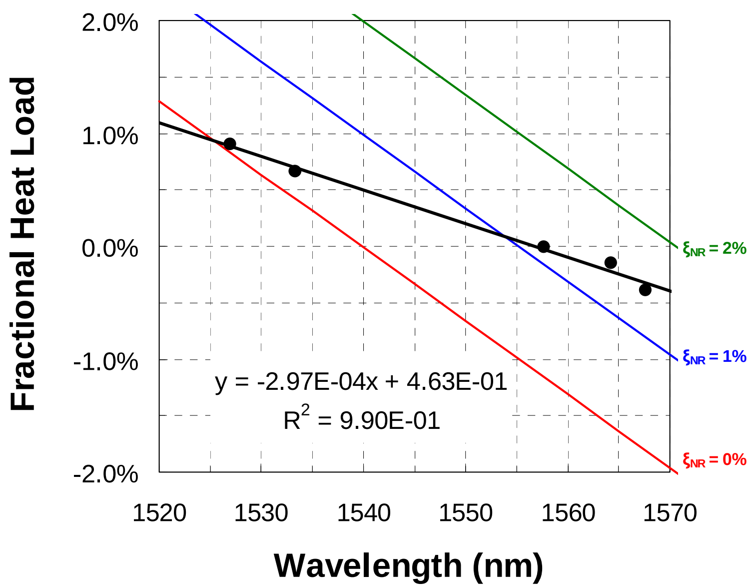

Fig. 4. Fractional heat load as a function of pump diode wavelength. The three diagonal lines are the expected lines for nonradiative contributions, ξ_{NR}, of 0%, 1%, and 2%.

4. Conclusions

Optical cooling has been observed for the first time from the $^4I_{13/2}$ state of erbium (III) in $Er^{3+}:KPb_2Cl_5$. The maximum observed cooling efficiency was 0.38% at 1567.6 nm. The nonradiative fractional heat load was for pumping into this state was found to be 1.1%, but the wavelength dependence of the overall heat load suggests the importance of other excited states. The low heat loads at all wavelengths suggest the possible use of this material system in resonantly-pumped eyesafe lasers.

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